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Detection and identification of nitrogen defects in nanodiamond as studied by EPR

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ABSTRACT

Electron paramagnetic resonance (EPR) and electron spin echo (ESE) at X-band and at high-frequency W-band (95 GHz) have been used to study defects in natural diamond nanocrystals, detonation nanodiamond (ND) with a size of ~4.5 nm and detonation ND after high-temperature, high-pressure sintering with a size of ~8.5 nm. Atomic nitrogen centers N^0 and nitrogen pairs N_2^+ have been detected and identified and their structure has been unambiguously determined by means of the high frequency EPR and ESE in natural diamond nanocrystals. In detonation ND and detonation ND after sintering atomic nitrogen centers N^0 have been discovered in nanodiamond core. In addition EPR signal of multi-vacancy centers with spin 3/2 seems to be observed in diamond core of detonation ND.

1. Introduction

The nanodiamond (ND) particles formed in the detonation of strong explosives, the so-called detonation ND, are of particular interest. The detonation NDs are characterized by a narrow size distribution with a sharp maximum at 4–5 nm and each particle consists of a core with an ordered diamond lattice and a shell. The surface and core shell structure of synthetic ND has been recently characterized by solid-state nuclear magnetic resonance (NMR) spectroscopy [1]. According to this NMR-based model the ND particle has a diameter of 4.8 nm and contains close to 10 000 carbon and 200 nitrogen atoms. About 40% of carbons are in the 3.6-nm diameter ordered crystalline diamond core and ~60% of carbons are in a seven-layer-thick, partially disordered shell. The ND surface carbons are bonded to H and OH groups. Unpaired electrons were shown to be not dangling bonds at the surface and are mostly located in the disordered shell, at distances between 0.4 and 1 nm from the surface, with a density of ~40 unpaired electrons per particle. Most nitrogen was shown to be located in disordered shell. About 8% of all carbon was suggested to be within 0.3 nm from the unpaired electron and thus unobservable by NMR.

ND doping processes, formation and structure of intrinsic and impurity defects differ from those in bulk diamonds. In particular, the theoretical studies have shown that nitrogen impurities in ND seem to be metastable in contrast to bulk diamonds [2].

Electron paramagnetic resonance (EPR) is one of the most informative techniques for the diagnostics of defects in semiconductors at the molecular level [3]. The structure of many intrinsic and impurity defects in bulk diamond crystals was determined by means of EPR [4].

Nitrogen (N) is the main impurity in diamonds and the form in which N is present in diamonds largely determines their properties and serves as the leading factor of the diamond classification. N creates various paramagnetic centers in a diamond and exists as individual atoms and N clusters [4]. Recently, a great interest has been inspired by the studies of nitrogen-vacancy centers (NV defects) in a diamond, for which the magnetic resonance on single defects was successfully observed at room temperature, [6] letting one even to speak of a "diamond era of spintronics" [7].

In this paper high-frequency continuous-wave (cw) EPR and pulse electron-spin echo (ESE) at W-band (94 GHz), have been used to study detonation ND with a size of ~4.5 nm and detonation ND after pressure sintering with a size of ~8.5 nm. The main goal of the study is to find EPR spectra of N related paramagnetic centers within the diamond core of detonation ND. The EPR spectra of isolated N donors N^0 have been observed in detonation ND after high-temperature and high pressure sintering in our recent publication [8], but the problem whether N donors are stable in detonation ND still remain unsolved.

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